Formaldehyde columns from the Ozone Monitoring Instrument:
Urban vs. background levels and evaluation using aircraft data and a global model

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1. Introduction

Tropospheric vertical column (Ω [molec. cm^{-2}]) measurements of formaldehyde (HCHO) and nitrogen dioxide (NO_2) from space-borne sensors offer constraints on the sources and photochemical processing of VOC (volatile organic compounds) and NO_X ($NO+NO_2$). Quantitative interpretation of satellite column data requires error characterization and consistency evaluation against other data sets. We evaluate measurements of Ω_{HCHO} from the Ozone Monitoring Instrument (OMI) against aircraft measurements and columns simulated by the GEOS-Chem chemical transport model. Ongoing work involves applying OMI Ω_{HCHO} and Ω_{NO2}, with GEOS-Chem, to investigate ozone production and variability across the U.S.

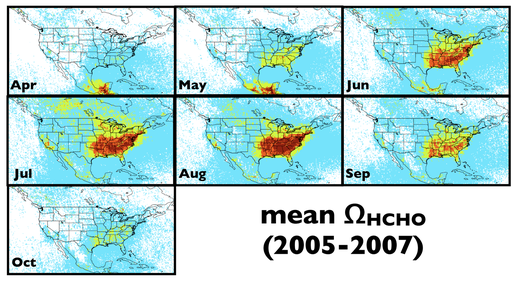
2. Spatial and temporal gradients in HCHO and NO_2

OMI:

- UV/Vis spectrometer on NASA's Aura satellite
- 13:45 local overpass
- Global coverage daily
- High spatial resolution: (13×24km^2 at nadir) provides more cloud-free scenes than predecessors; better sampling statistics

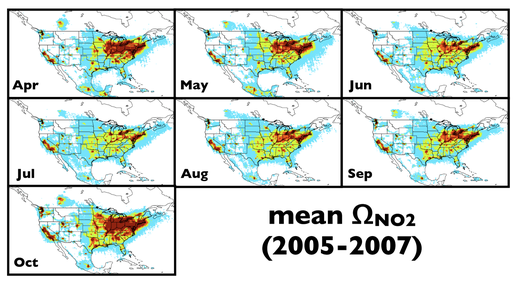
HCHO Retrievals

- Clear seasonal cycle in Ω_{HCHO} reflects temp., radiation and HCHO yield from biogenic VOC
- No major enhancements over urban areas
- Dry-season biomass burning visible in Yucatan

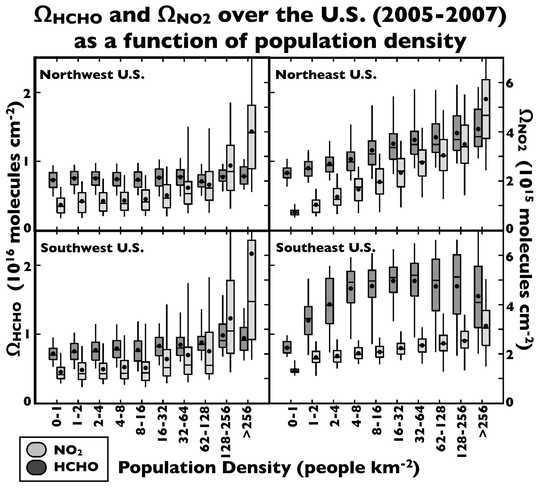


NO_2 Retrievals

- NO_2 columns mainly reflect anthropogenic emission sources; particularly fossil fuel combustion
- NO_2 lifetime decreases in summer with increased photolysis



Urban-Rural Gradients & Regional Variability



- Ω_{NO2} increases strongly over the most densely populated areas.
- No corresponding relationship is detectable for Ω_{HCHO} except over the U.S. Northeast (possibly U.S. Southwest?)
- In the U.S. Southeast high isoprene emissions → high Ω_{HCHO}
- Here we evaluate the fidelity of the satellite sensor in resolving such gradients for HCHO

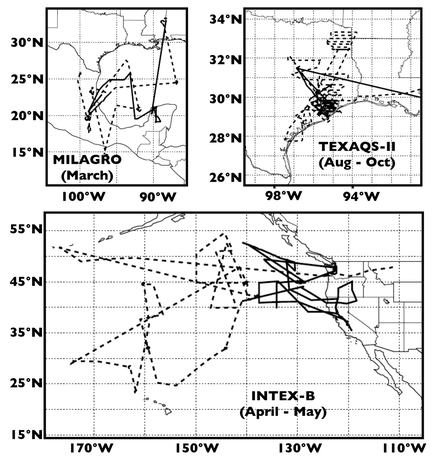
3. Airborne HCHO measurements

Campaign	Platform[a]	Map Symbol	Measurement Technique[b]	Limit of Detection	Measurement Uncertainty
TEXAQS-II	Piper Aztec	——	FHR	50-120pptv	10%
TEXAQS-II	WP-3D	- - -	DFGAS	20-30pptv	13%
MILAGRO	C-130	——	DFGAS	30-55pptv	13%
MILAGRO	DC-8	- - -	TDLAS	20-30pptv	13% - 15%
INTEX-B	C-130	——	DFGAS	20-30pptv	13%
INTEX-B	DC-8	- - -	TDLAS	20-30pptv	13% - 15%

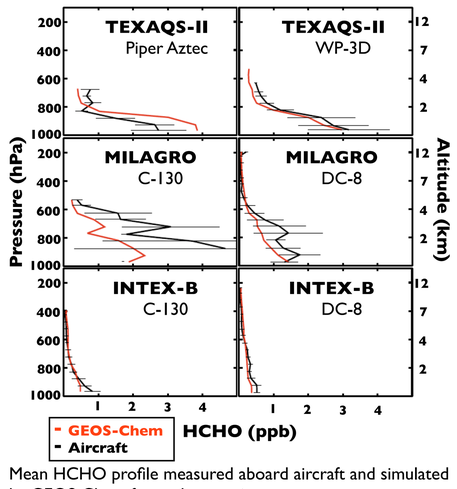
[a]measurements on board Piper Aztec made by University of Houston; all others made by NCAR
[b]FHR=fluorometric Hantzsch reaction spectroscopy; DFGAS=difference frequency generation absorption spectrometry; TDLAS=tunable diode laser absorption spectroscopy

2006 Campaigns

- *TEXAQS-II*: chemical processing, emissions and air quality in Texas airsheds
- *MILAGRO* and *INTEX-B*: pollution outflow and transport from Mexico City and Asia
- For comparison with OMI Ω_{HCHO} we restrict flight data to times bracketing OMI overpass (12:00-15:00 local time)



Flight tracks for flights used in this evaluation between 12:00 - 15:00 local time; see key in table above



Mean HCHO profile measured aboard aircraft and simulated by GEOS-Chem for each campaign

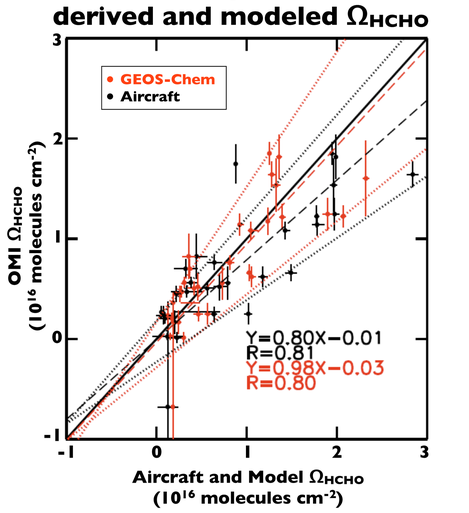
In situ Ω_{HCHO} Determination

- On average HCHO profile shape is well-captured by GEOS-Chem
- We integrate HCHO within each flight's vertical limits then extrapolate to the surface and to the tropopause
- Ω_{HCHO} calculated this way from modeled profiles correlates well with with Ω_{HCHO} from full 3D model grid: Y=1.1X−0.02; R=0.98 providing support for the method

4. OMI Ω_{HCHO} evaluation

- OMI Ω_{HCHO} correlates well with Ω_{HCHO} extrapolated from aircraft measurements and GEOS-Chem simulations (R=0.8)
- Low OMI/GEOS-Chem bias possibly due to plume-sampling focus of many flights vs. dilution over pixel/grid footprint
- Negative OMI Ω_{HCHO} values likely result from error minimization in fitting the retrieved radiances (only occurs where HCHO is very low)

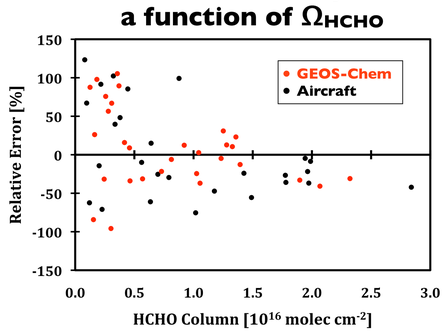
OMI Ω_{HCHO} compared to aircraft-derived and modeled Ω_{HCHO}



Dashed lines indicate best fit (regressions inset); dotted lines indicate 95% confidence intervals for regression

- OMI's mean bias is < 2% relative to aircraft measurements (full data set), −17% where Ω_{HCHO} > 4.0E15 molec. cm^{-2}, but this bias is within the retrieval uncertainty
- OMI's mean bias relative to GEOS-Chem is −8% (full data set), −10% where Ω_{HCHO} > 4.0E15 molec. cm^{-2}

OMI uncertainty as a function of Ω_{HCHO}



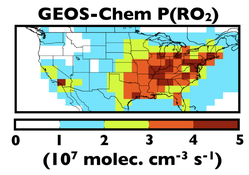
5. Summary

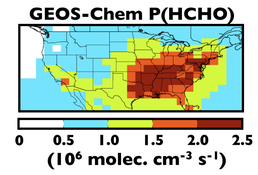
- Aircraft HCHO measurements from *MILAGRO*, *TEXAQS-II* and *INTEX-B* provide a challenging comparison for OMI and GEOS-Chem as many flights focused on sampling polluted urban and biomass-burning plumes, which may be diluted by averaging over the satellite/model footprint (up to 28×150 km^2 and 2°×2.5°)
- Still, both OMI and GEOS-Chem Ω_{HCHO} correlate well with HCHO observations from aircraft (R=0.80 and 0.81).
- Given sufficient averaging over time and space to reduce random noise in the retrieval, OMI is able to capture spatial and temporal gradients in HCHO within instrument uncertainty.

6. Ongoing Research

How does OMI Ω_{HCHO} relate to Ozone Production?
(all plots below show mean values for summer months during 2005)

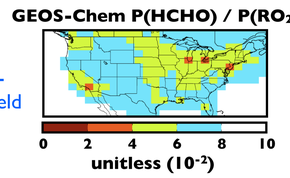
- Ω_{HCHO} closely related to peroxy radical production rate ($P(RO_2)$)
  - dependent on VOC-OH reactivity and HCHO yield of local VOC mix
  - $P(RO_2) = \Sigma\, k_i[OH][VOC_i]$
  - $P(HCHO) = \Sigma\, \alpha_i k_i[OH][VOC_i]$

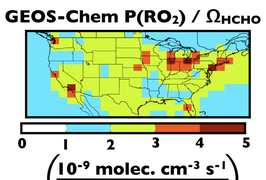




- We use GEOS-Chem to examine how $P(RO_2)$ relates to Ω_{HCHO}

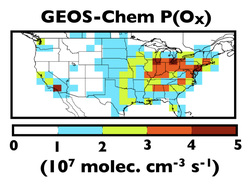
This gives reactivity-weighted HCHO yield for local VOC mix

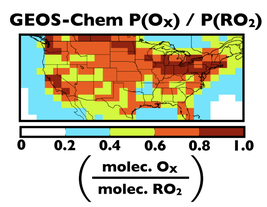




- Note higher $P(RO_2)$ per HCHO yield in urban areas

- $P(RO_2)$ is related to ozone production rate $P(O_X)$ by:
  - $RO_2 + NO \rightarrow NO_2 + RO$
  - $NO_2 + h\nu \xrightarrow{O_2} NO + O_3$





Compare $P(O_X)$ to $P(RO_2)$

- Not every peroxy radical makes ozone
  - Where NO_X/VOC is low, some RO_2 removed by HO_2–RO_2 reactions
  - Where NO_X/VOC is high, RO_2 typically makes O_3 before being removed

Acknowledgements

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